Evolution to carbonated compounds of phases developed on ternary systems materials

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Abstract
The incorporation of supplementary cementitious materials to the cement industry is an alternative to reduce consume of large amounts of raw materials and gives up a huge spectrum of blended cements that have been noted not only for its properties of reducing energy consumption and CO_2 emission but also for its well known durability properties.

In this research work we evaluate ternary systems from CAC/FA/C$ mixtures, focusing on their durability. Selected formulations in the ternary system CAC/FA/C$ hydrated and carbonated have been studied at 14 and 90 days of carbonation time. The carbonation process of ettringite phases and calcium aluminate hydrates proceeded from different formulations, i.e. calcium aluminate cement, fly ash predominance, and calcium sulphate is analysed and discussed by means of infrared spectroscopy, x-ray diffraction but also mechanical properties of samples. The analysis of the results have shown that developed hydrated compounds depend on formulation; after carbonation process, the ettringite decomposition can promote metastable calcium carbonate polymorphs (aragonite and vaterite) due to inorganic compounds (aluminium hydroxide, gypsum, etc) presence. Long term carbonation of the blended samples analysis by Raman spectroscopy allows the identification of a new hydrated phase with carbonate, sulphate and calcium ions in its structure.

Originality
This paper describes for the first time a study of the durability of different selected formulations in the ternary system CAC/FA/C$ which substitutes the Portland cement by by-products. On the hydrates characterization, the Infrared and Raman spectroscopies allow the identification of differentiate ettringite structures.

Chief contributions
The carbonation of the hydrated samples produces ettringite decomposition as well as reaction of CO_2 with minor hydration products i.e. C_3AH_6, calcium monosulfoaluminate, hemicarboaluminate and C_2ASH_8 - developed phases depending on the selected initial formulation. Two metastable calcium carbonate polymorphs (vaterite and aragonite) with different morphologies development can be related with gypsum and AH_3 presence.

Keywords: *ternary systems, ettringite carbonation*

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Introduction

The incorporation of supplementary cementitious materials to the cement industry is an alternative to reduce consume of large amounts of raw materials and gives up a huge spectrum of blended cements that have been noted not only for its properties of reducing energy consumption and CO_2 emission but also for its well known durability properties [Macphee D E., 2006]. In the near future, the sustainability will be the main driver for innovation in research on materials; moreover, an increase range of supplementary cementitious materials but also new clinker types will emerge over the coming years contributing to lower environmental impacts [Karen L. Scrivener, R. James Kirkpatrick, 2008].

In the same line of interest, advanced materials research on new cementing systems, as high sulphate clinkers, has also recently focused on ettringite rich products to develop materials with special properties [Chatterji, S., Jeffery, J. W., 1963]. Currently, as a precursor to the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), the blend of Portland cement (PC), calcium aluminate cement (CAC) and a type of calcium sulphate – i.e. anhydrite, hemihydrate or gypsum - is on special attention of researchers [Brooks, S.A., Sharp, J.H., 1990; Lamberet S., 2005; Fernández-Carrasco L., 2008; Fernández-Carrasco L., Martínez-Ramírez S., 2009]. The products based on ettringite have a broad range of uses: formulations with water contents near the minimum requirement to ensure plasticity are widely used in proprietary floor screeds and repair materials. The compressive strength depends on formulation but it is comparable with those achieved by sulphate-free CAC cements. Actually, new attempts to obtain ettringite-rich materials by the incorporation of fly ash as an alternative high sustainable ternary systems have been just investigated obtaining clearly good products [Fernández-Carrasco, L. 2009], but next step is that some durability studies are required in order to establish the long term composition and mechanical characteristics.

In this research work, the carbonation process of ettringite phases and calcium aluminate hydrates proceeded from different formulations, i.e. calcium aluminate cement, fly ash predominance, and calcium sulphate is analysed and discussed by means of infrared spectroscopy, x-ray diffraction but also mechanical properties of samples.

Experimental

A fly ash (Type F according to the ASTM classification), an Electroland CAC and calcium sulphate 2-hydrate (Panreac PRS-CODEX) were used in this research as raw materials.

The formulations were prepared in a mixer by blending the raw materials during 1 hour at 9 rpm (Table 2). The "water/binder" ratio used was 0.6 and the samples were prepared as described in a previous work [Fernández-Carrasco, L. 2009]. These hydrated pastes were submitted to a carbonation process in a chamber of 50x30x20 cm dimensions within 4% of CO_2 in air, 20 º C of temperature and 75 % of relative humidity. The samples were analysed after 14 and 90 days of carbonation time.

A PHILIPS PW 2400 X-ray fluorescence spectrometer with a PW 2540 VTC sample changer was used to determine the chemical composition of the materials (see Table 1). The mineralogical composition of the hydrated and carbonated materials was performed by an X-ray diffractometer (XRD) with a Siemens D500 instrument and an FTIR- Bomem MB-120 Fourier transform infrared spectrophotometer with a frequency range of 450 to 4000 cm^{-1} were used. KBr pellets procedure was used for FTIR analysis. A 1800 Jeol scanning electron microscopy (SEM) was used to study the microstructure of carbonated pastes.

Table 1. Chemical Composition of raw materials

	loss on ignition	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	K_2O	Na_2O
CAC	0.36	40.52	34.89	2.94	12.91	0.5	0.06	0.14
Fly ash	1.27	25.84	5.93	41.49	20.76	1.22	1.37	---

Results and discussion

As was reported in a previous work [Fernández-Carrasco, L. 2009], the main crystalline hydration product of the reactions in the S1 to S4 studied systems was ettringite. Apart from ettringite, the sample S4 presented a high portion of non reacted gypsum; presumably an excess of C$ was used in the initial mixture. The samples S5 and S6 -with major portion of CAC- presented minor ettringite content but in addition also presented C_3AH_6; and the broad diffraction lines between 2θ = 6-16° indicated calcium monosulfoaluminate and hemicarboaluminate. The diffraction lines for aluminium hydroxide polymorphs are observed only in the diffraction patterns of samples with high content (S5 and S6). Moreover, the samples S5 and S6 presented a very low portion of C_2ASH_8.

The carbonation of samples conducted to an evolution of hydrated phases, due to the chemical reactions of them with CO_2, towards the formation of calcium carbonate, gypsum and aluminium hydroxide. The Figures 1 and 2 present the diffractograms of hydrated and carbonated samples -14 and 90 days, respectively.

Then, the carbonation of samples gives up to the evolution of ettringite. At 14 carbonation days, the diffraction lines of the ettringite decrease in the relative intensity but at 90 carbonation days no signals of ettringite are shown. Other minor hydration products, i.e. C_3AH_6, calcium monosulfoaluminate, hemicarboaluminate.and C_2ASH_8, also react totally with CO_2.

The crystalline detected products were calcium carbonate, aluminium hydroxide and gypsum. At 14 carbonation days, the main detected calcium carbonate polymorph was vaterite; but the samples S3 y S4 presented aragonite in major portion than vaterite. In the diffractogram of sample S5 were observed minor relative intense diffraction lines due to calcite and aragonite (Figure 5).

At 90 days, an important increase in the presence of vaterite was observed in samples S1, S2, S5 and S6. Samples S1 and S2 also increased in aragonite. On the other hand, the main calcium carbonate polymorph detected at 90 days carbonation time for samples S3 and S4 was aragonite (Figure 6).

At 14 carbonation days, the diffraction lines due to the presence of aluminum hydroxide were observed in the diffractograms of all the samples. However, at 90 carbonation days, aluminium hydroxide was only detected in samples S5 and S6. The formation of a sulphate type compound, probably gypsum was also detected by XRD at 14 carbonation days in samples S1 to S5; however more research need to be done on this aspect. Major portion of this sulphate was detected at 90 days, mainly in samples S4 and S3 (Figures 5-6).

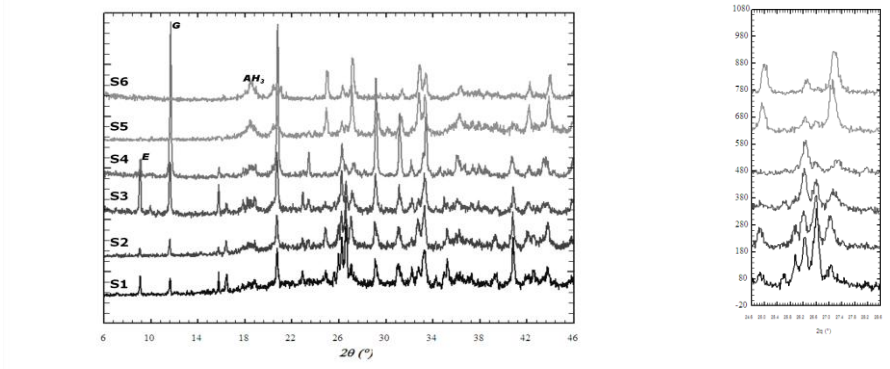

Figure 1: X Diffraction patterns of samples at 14 days of carbonation time. Detail of carbonates diffraction lines at 26,4 º (aragonite) and 27,1º (vaterite)

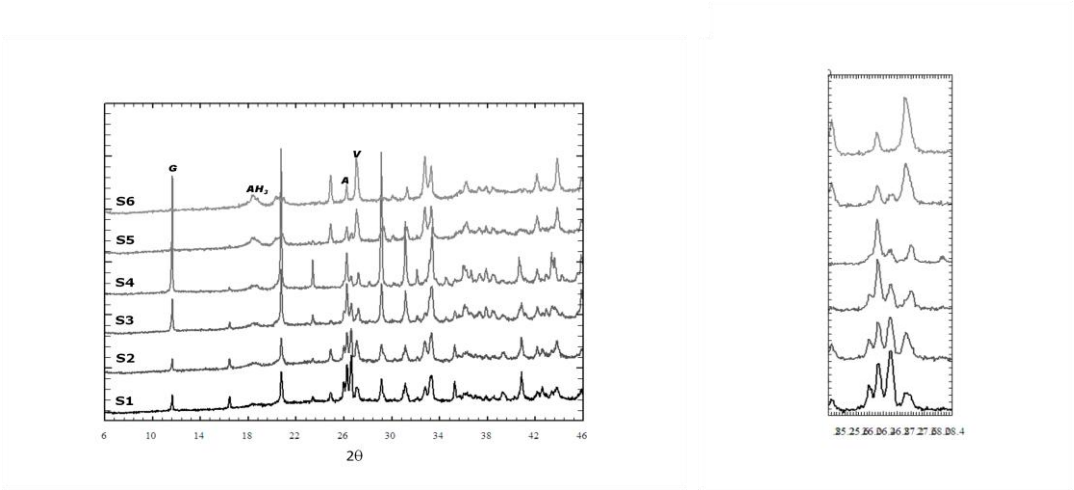

Figure 2. X Diffraction patterns of samples at 90 days of carbonation time. Detail of carbonates diffraction lines at 26.4 º (aragonite) and 27.1º (vaterite)

The IR spectrums of S1 to S4 show clearly the ettringite presence throughout the bands at 3638, 3525 and 3430 cm^{-1} and near to 1665, 1110, 988 and 855 cm^{-1}; other absorption bands near to 600 and 536 cm^{-1} are assigned also to ettringite [Fernández-Carrasco, L. 2009, Bensted, J. 1982]. The IR spectrum of S1 and S3 samples presented a very slight absorption bands near to 1025 and 990 cm^{-1} indicating AH_3 presence. Moreover, the IR spectrum of S4 sample presented absorption bands due to gypsum, at 1690, 1620 and 670 cm^{-1} and the absorption band towards to 600 cm^{-1} is also due to the contribution of gypsum. It can be observed in S6 spectrum a weak waveband near to 3665 cm^{-1} characteristic of OH free frequency of cubic calcium aluminate hydrates, C_3AH_6; however, this absorption band was not evident in the spectrum of S5 sample. Both IR spectrums, S6 and S5, presented absorption bands towards 3620, 3525 and 3465 cm^{-1} due to aluminium hydroxide, gibbsite. An absorption band towards 3684 cm^{-1} (ν-OH free) could indicate presence of C_4AH_{13} [Volant J., 1966] and also an absorption band near 3640 cm^{-1} would indicate ettringite; moreover a band around 3673 cm^{-1} could be due to calcium monocarboaluminate. Nevertheless, we need to take into account that this spectrum area is very difficult to analyse due to the overlapping with the AH_3 absorption bands. Most important difference between S5 and S6 spectrums are the relative intensity of the absorption band sited near 1110 cm^{-1} – of major relative intensity in S5 sample spectrum; an anti-symmetrical stretching frequency of the sulphate ion (ν_3-SO_4) indicates the relative isolation of this ion in the hexagonal prism, although a greater degeneracy of the symmetry would result in more bands in this area of the spectrum of ettringite. The absorption bands near to 1025 and 970 cm^{-1} are assigned to AH_3. At lower frequencies, the aluminate bands towards 790 cm^{-1} (Al–O–H bending) and 530 cm^{-1} (ν-AlO_6) are not suitable for identification because C_3AH_6, monosulfoaluminate, C_4AH_{13} and ettringite present very close absorption bands.

IR spectrums of 14 days carbonated samples show a very broad absorption area between 3650 towards 3350 cm^{-1} with maximums near to 3621, 3525 and 3467 cm^{-1} due mainly to aluminium hydroxide, gibbsite (Figure 2). The spectras show a broad strong ν_3 carbonate bands between 1600–1300 cm^{-1} The ν_3-carbonate band is centred near 1480 cm^{-1} in S1, S2, S5 and S6 spectras, and towards to 1495 cm^{-1} in S3 and S4 spectras, respectively. The ν_1 carbonate bands appear near 876 cm^{-1} in the spectrum of samples S1, S2, S5 and S6 but close to 855 cm^{-1} in the spectrums of S3 and S4, depending on the developed calcium carbonate polymorph, assigned to vaterite and aragonite, respectively. In the samples it is also observed the ν_4 carbonate band at 713 and 700 cm^{-1}, clearly in the samples S3, S4, S5 y S6 and like a shoulder in the samples S1 and S2. These results would indicate that the main calcium carbonate polymorph formed is vaterite in samples S1, S2; aragonite is developed through carbonation of S3 and S4 samples and both polymorphs in S5 and S6.

At 90 days of carbonation, the spectras of samples S1 to S4 also show a very broad absorption area between 3650 towards 3350 cm^{-1} but some modifications can be observed in the maximum positions of the absorption bands with respect to the spectrums of 14 carbonation days samples; now, the maximums appear near to 3540, 3470, 3410 and 3245 cm^{-1} (Figure 3). However, the absorption bands due to AH_3 increase in spectras of S5 and S6 samples, with maximums at 3624, 3525 and 3468 cm^{-1}. The absorption bands due to carbonate compounds do not experiment an important modification –S1, S2, S5 and S6 present absorption bands at 1480 and 875 cm^{-1} while samples S3 and S4 at 1500 and 855 cm^{-1}, indicating the presence of same carbonate compounds –vaterite and aragonite, respectively; but they are higher in intensity at 90 days carbonation time showing a major portion of them (Figure 3).

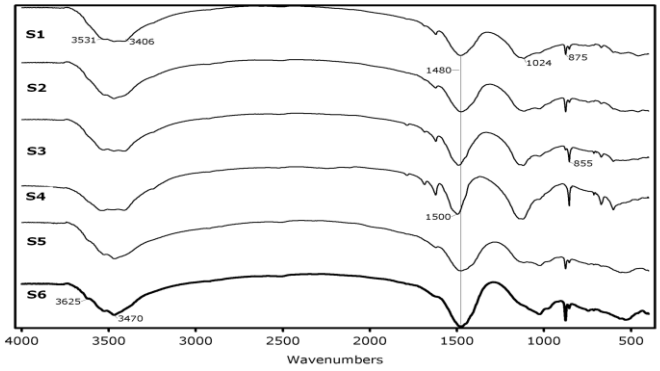

Figure 2. IR spectras of samples at 90 carbonation days.

The position of the absorption bands sited near to 3540, 3470, 3410, 3245, 1685, 1623, 1143, 1115, 670 and 600 cm^{-1} indicate the presence of a sulphate compound similar to gypsum. The intensity of the mentioned bands indicate major portion in S4 sample and then S3, minor in S1, S2 and S5, respectively (Figure 3). Moreover, the presence of 1025 cm^{-1} absorption band, indicating the aluminium hydroxide compounds presence, is specially noted in the spectrums of S6 and then S5 samples; but they are present in all spectrums.

Zhou and Glasser, 2001, studied ettringite stability under controlled relative humidity at 68 and 88 % in different solid forms, as powder and in pellets. Ettringite completely transformed to gypsum and vaterite, when it was in powder form, while only the exposed surface presented complete dissolution in pellets. In the exposed pellets, the layers beneath revealed partial dissolution and transformation to monophase, while in the deepest layer, ettringite remained intact. In the present study – carbonation of solids as powder and at 75 % of RH, a different developed calcium carbonate was analyzed depending on the formulation; samples S1, S2, S5 and S6 presented mainly vaterite; but samples S3 and S4 presented important amounts of aragonite. The carbonation of samples also produced the formation of aluminum hydroxide and hopefully gypsum. The formation of that sulphate type compound, probably gypsum was also detected by XRD in carbonated samples S1 to S5 but mainly in S3 and S4; however more research needs to be done on this aspect. In such context, it has been reported about the existence of a carbonate analogue of SO_4-AFt -firstly described by Carlson 1967, as CO_3-AFt, but the synthesis of this compound presented some difficulties. Poellman et al. 1990 and Barnett et al. 2001, indicated the existence of possible solid solutions formed between SO_4-AFt and CO_3-AFt. Moreover, Zhang et al. 2001, explained that the ettringite itself undergoes union exchanges in which part of its sulphate is replaced by carbonate; they suggest that ettringite undergoes significant ion exchange, of CO_3 for SO_4, prior to its decomposition and thus also buffers the paste against carbonate penetration.

Another aspect to be in present is that during the hydration process of cements if waste ions are mixed with, several types of waste ion interactions may occur in the cement microstructure: chemisorb, precipitate, form a surface compound to any of several cement phases surfaces, form inclusions or be chemically incorporated into the cement structures, or have simultaneous occurrence of several of these situations [S.J. Barnett, C.D. Adam, A.R.W. Jackson, 2001]. The ettringite structure can withstand modest deviations in composition without a change in structure. This compositional change occurs on the crystal chemical level in the form of ionic substitution; the ions available for substitution in the ettringite structure are Ca^{+2}, Al^{3+}, SO_4^{2-} and OH^-. The examination of ettringite group structures provides information on some natural and, therefore, stable ionic substitutions possible in the structure [Taylor H.F.W., 1973]. The aluminium site accommodates a variety of trivalent and tetravalent cations. Then, the carbonation of ettringite based systems that incorporate waste materials should not be clearly modified due to the ionic substitutions in the structure.

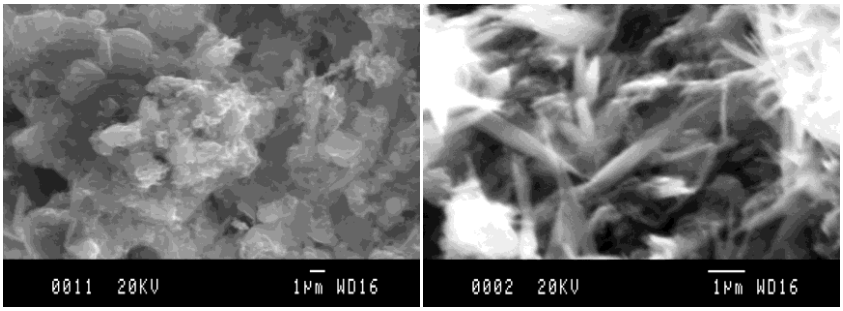

Figure 3. Dense and needle morphology of carbonates.

Conclusions

This paper describes the carbonation of ettringite and minor hydration products i.e. C_3AH_6, calcium monosulfoaluminate, hemicarboaluminate and C_2ASH_8 - developed phases depending on the selected initial formulation CAC/FA/C$- towards the formation of calcium carbonate, gypsum and aluminium hydroxide.

No signals of ettringite are shown at 90 days carbonation time. Other minor hydration products, i.e. C_3AH_6, calcium monosulfoaluminate, hemicarboaluminate.and C_2ASH_8, also react totally with CO_2. Two calcium carbonate polymorphs (vaterite and aragonite) with different morphologies development can be related with gypsum and AH_3 presence.

Depending on the initial composition, the samples S1, S2, S5 and S6 presented mainly vaterite; but samples S3 and S4 presented important amounts of aragonite. The carbonation of samples also produced the formation of aluminum hydroxide and hopefully gypsum.

As was mentioned, the presence of aluminium hydroxide was observed in the samples at 14 days; however, at 90 carbonation days, was only detected in samples with major initial CAC - S5 and S6. Then, AH_3 evolves or reacts due to carbonation.

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